UnLOHCked

UNlocking the potential of LOHCs through the development of KEy sustainable and efficient systems for Dehydrogenation
HORIZON-JTI-CLEANH2-2022-02-05

Valérie Meille, Catherine Pinel, Nuno Rocha Batalha, Laurent Piccolo, Chloé Thieuleux

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IRCELYON - CP2M

May 2023

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INSTITUT DE RECHERCHES SUR LA CATALYSE ET L'ENVIRONNEMENT

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Context of LOHC

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H0-BT/H12-BT pair
Catalysts
Bimetallic catalysts
Single-atom catalysts…
…or nano-clusters
Hsp supports for hydrogenation
Hsp supports for dehydrogenation
Conclusion
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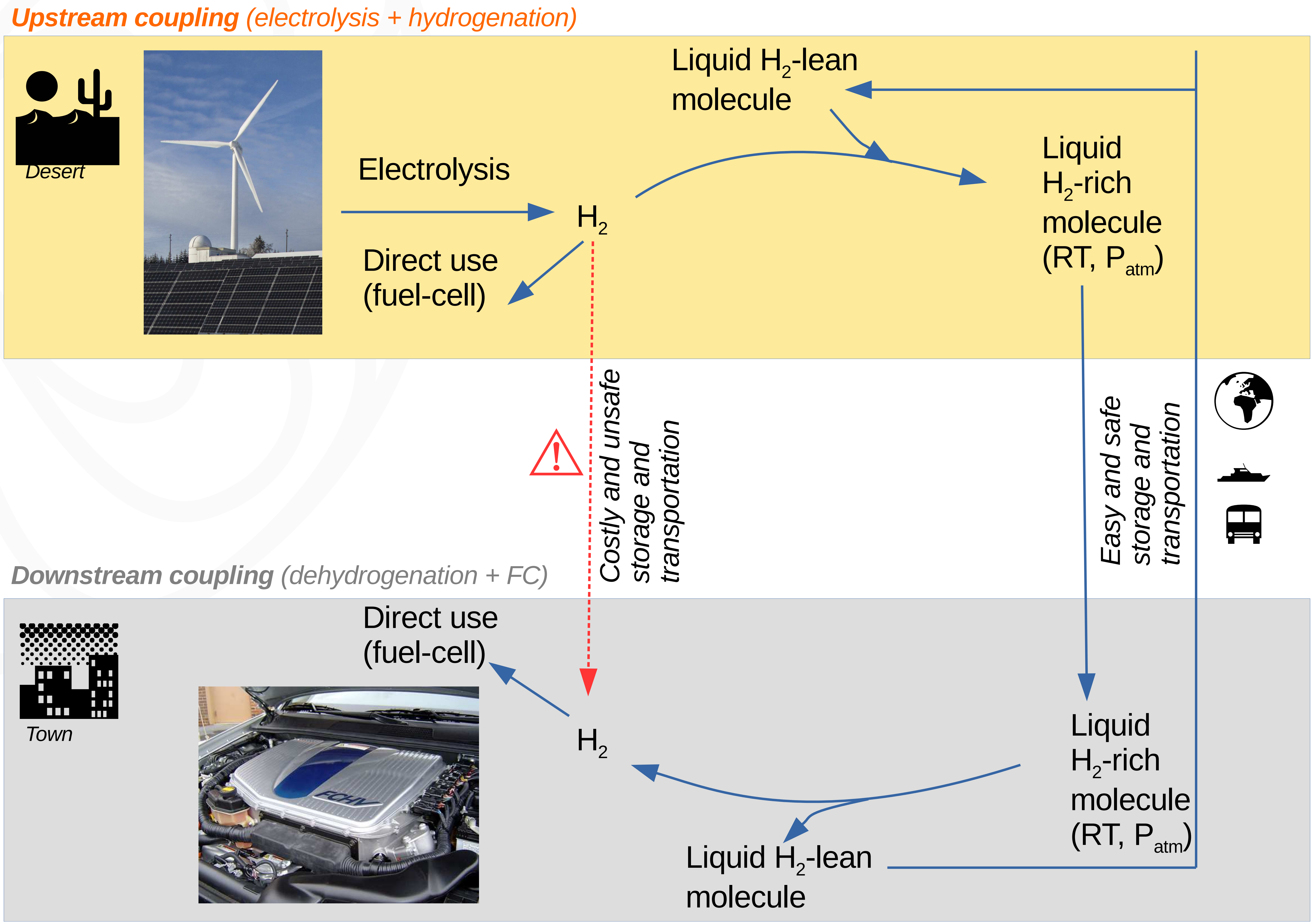

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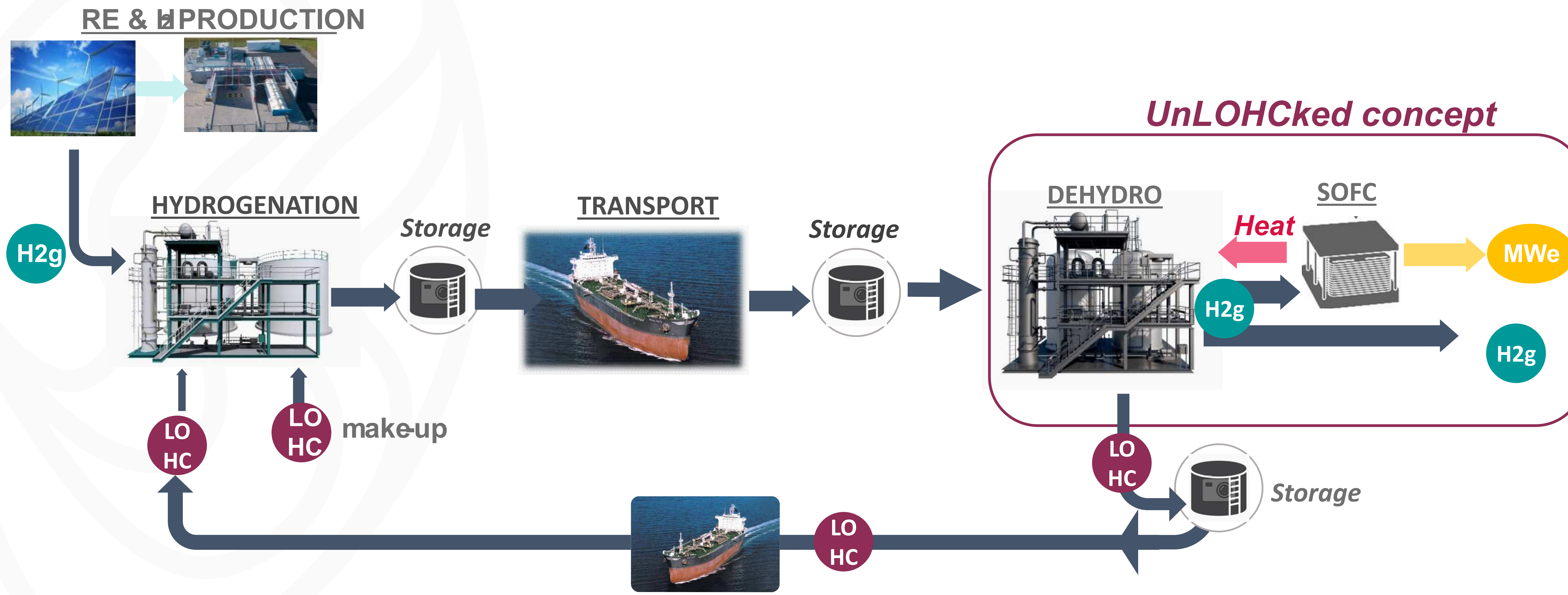

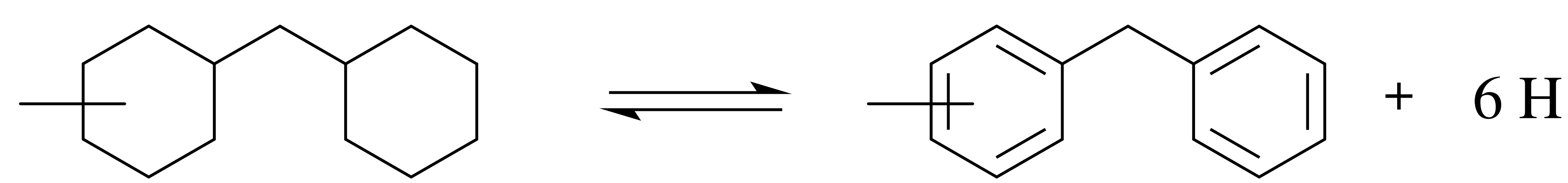

H12-BT/H0-BT pair

Methodology

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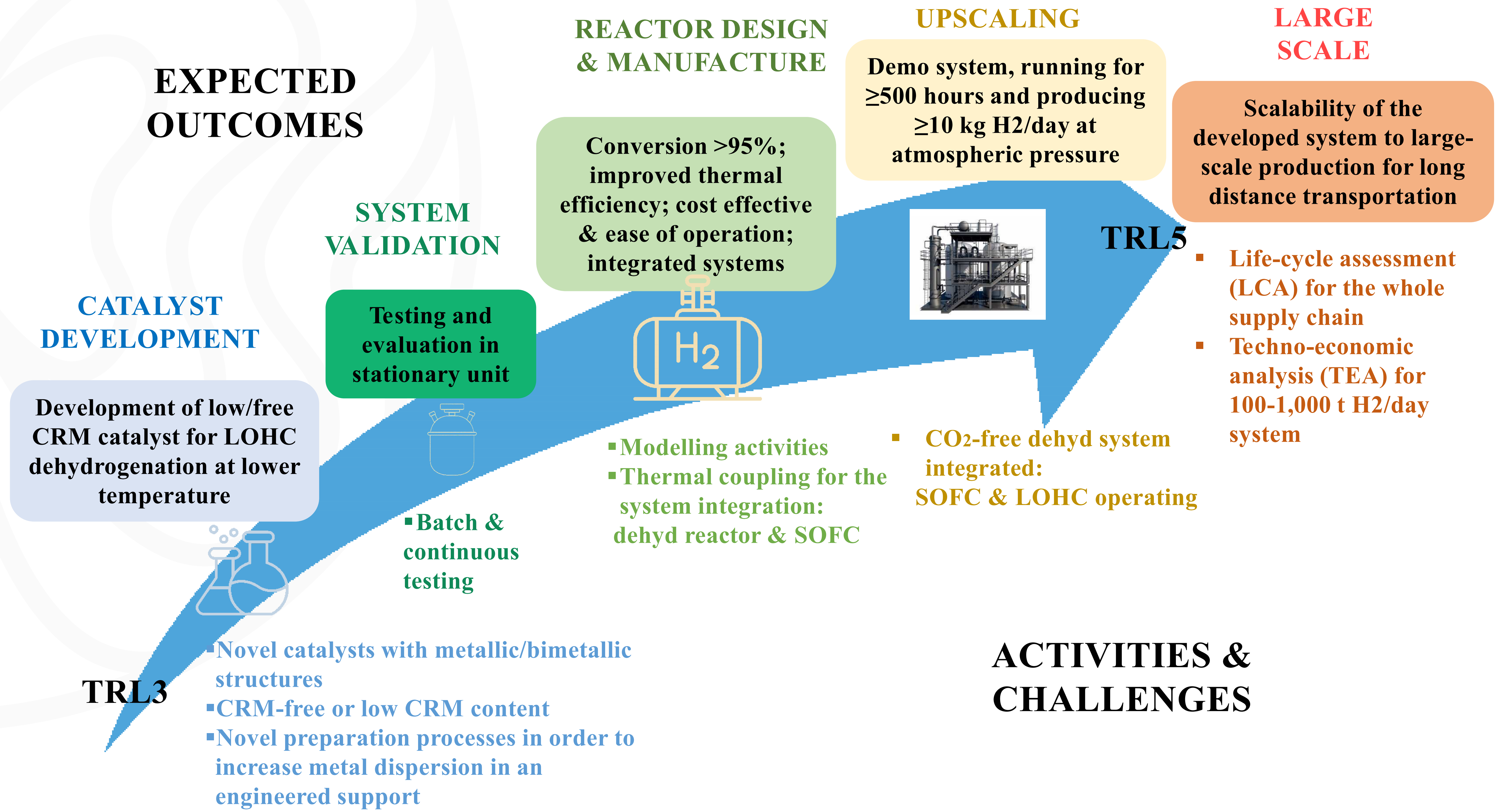

Tasks

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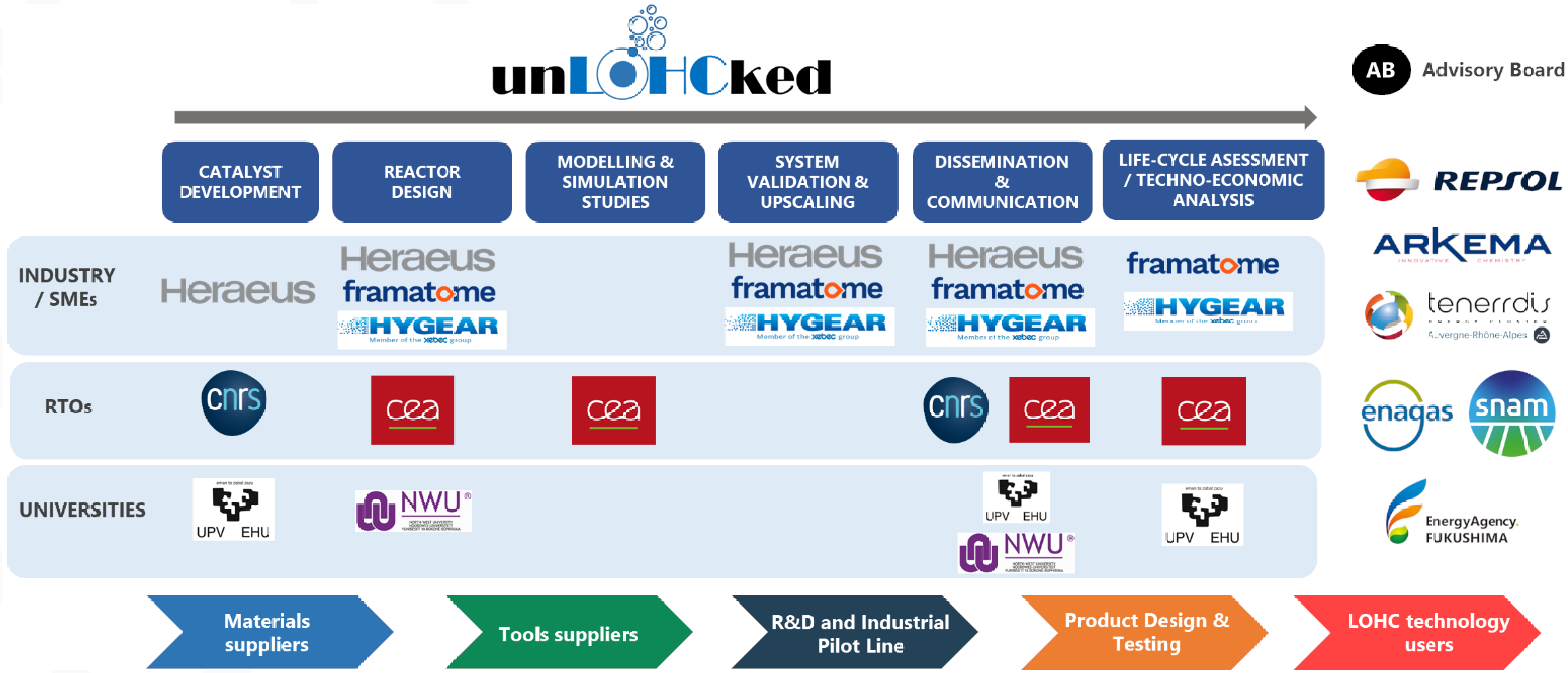

Dehydrogenation issues

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- Only PGM catalysts are highly active and selective
- The dehydrogenation enthalpy is high and the reaction must be performed at high T°C (250-300°C)
- Some by-products of the reaction (traces) avoid the complete cycling dehydrogenation/hydrogenation
- Some catalyst deactivation may occur

Dehydrogenation reactor

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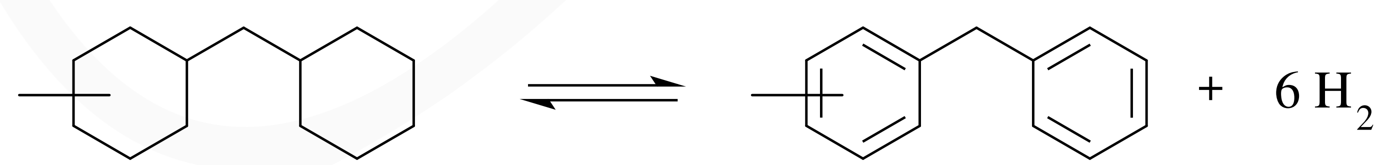
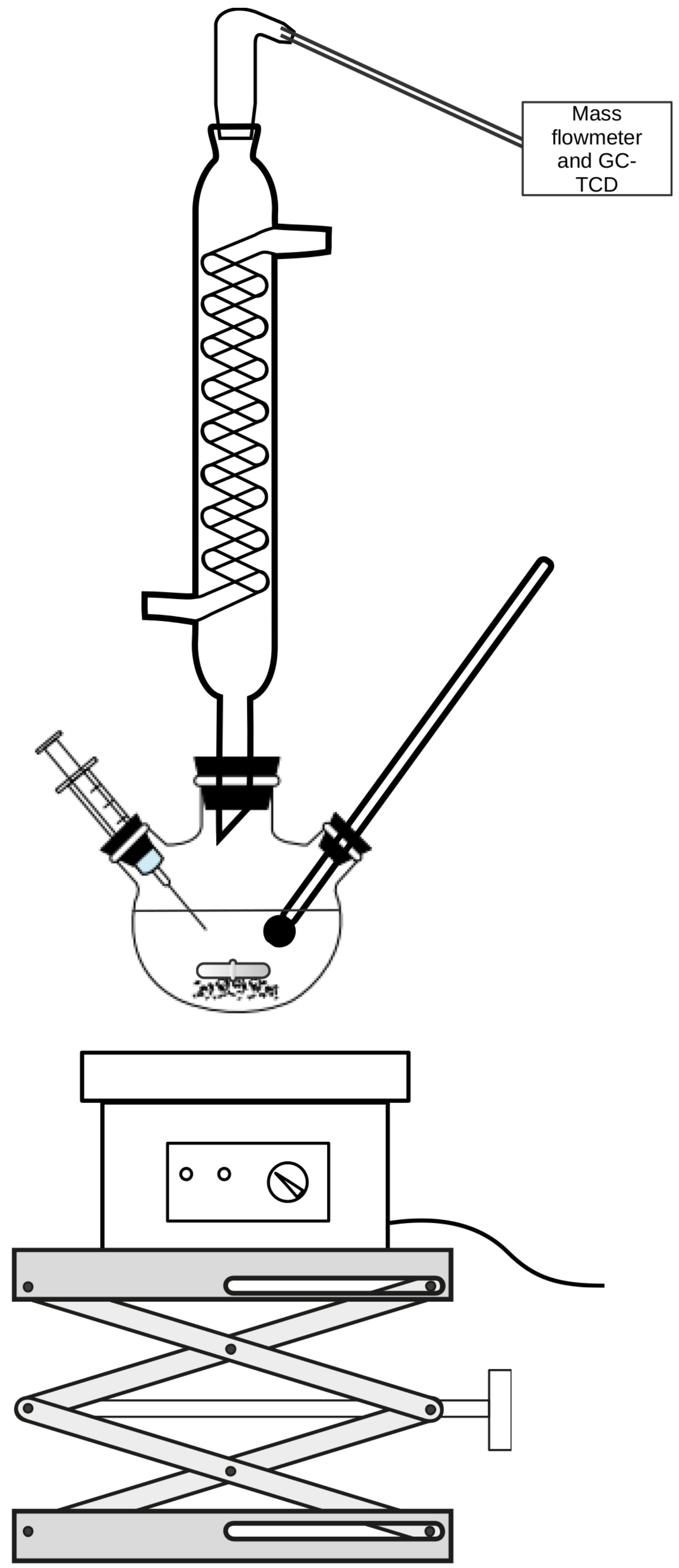
Test in stirred reactors (G/L/S) with continuous removal of hydrogen (H_2 flow rate measurement).

Different temperatures

Different catalyst loadings

No solvent





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Liquid phase analysis

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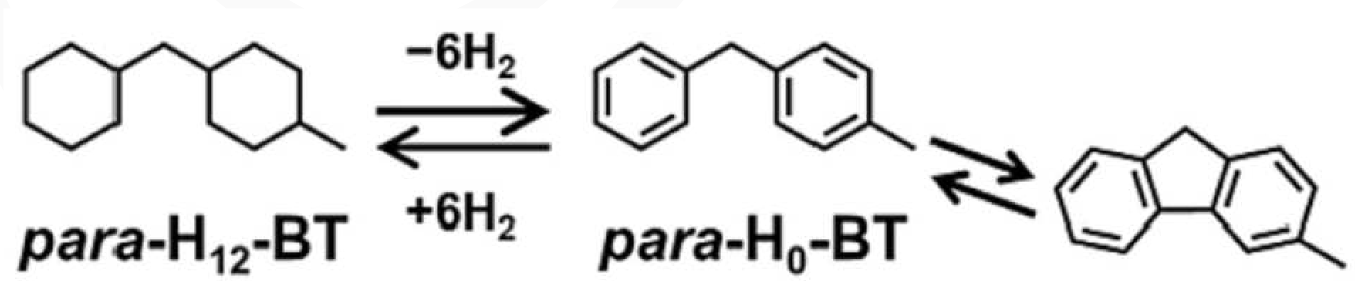
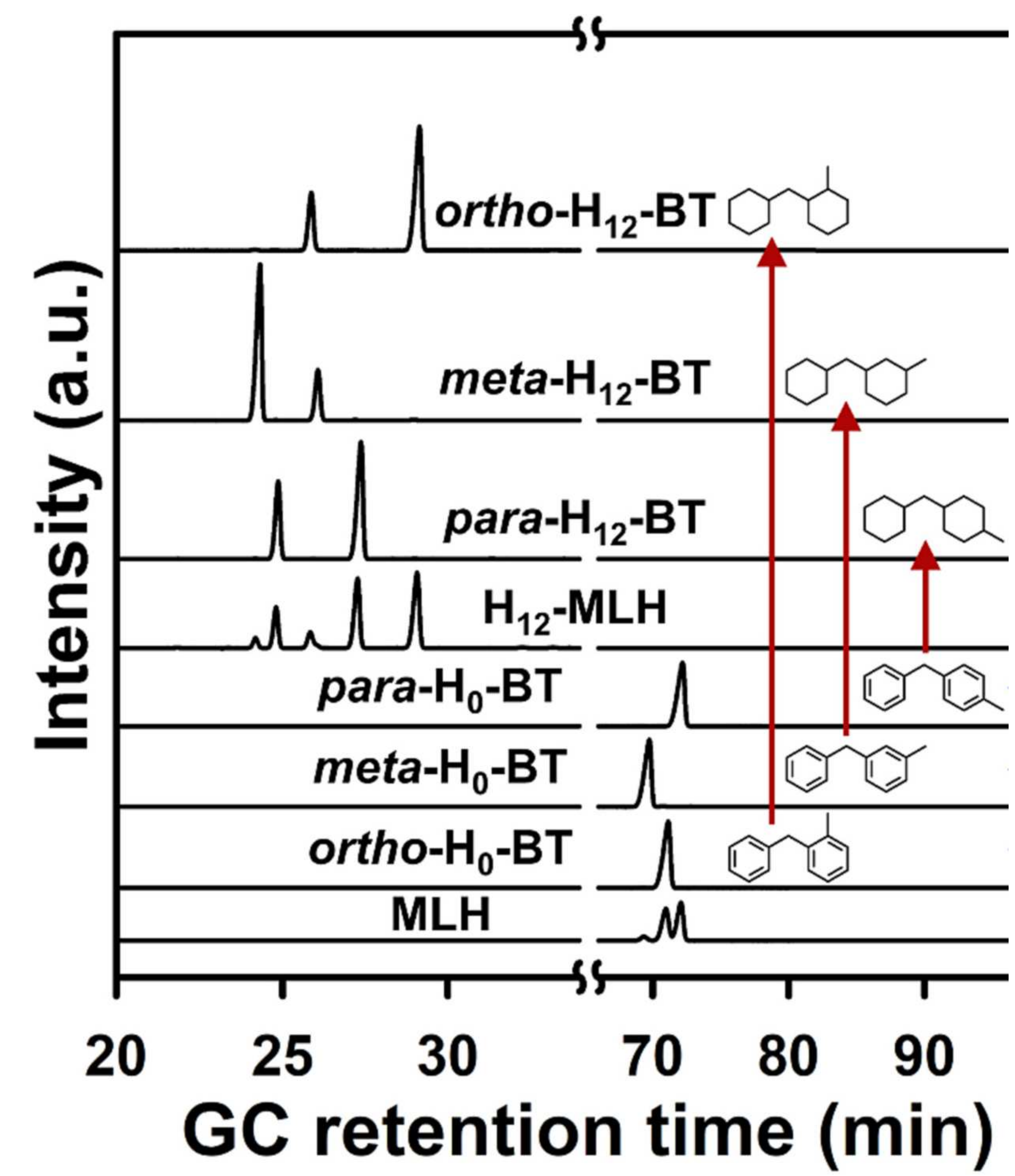
Analysis of LOHC+ and LOHC- molecules by GC
BUT
many isomers at each dehydrogenation degree.

Known by-product:
methyl-fluorene





Kim, T. et al. Journal of Energy Storage, 2023, 60, 106676

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H0-BT/H12-BT pair

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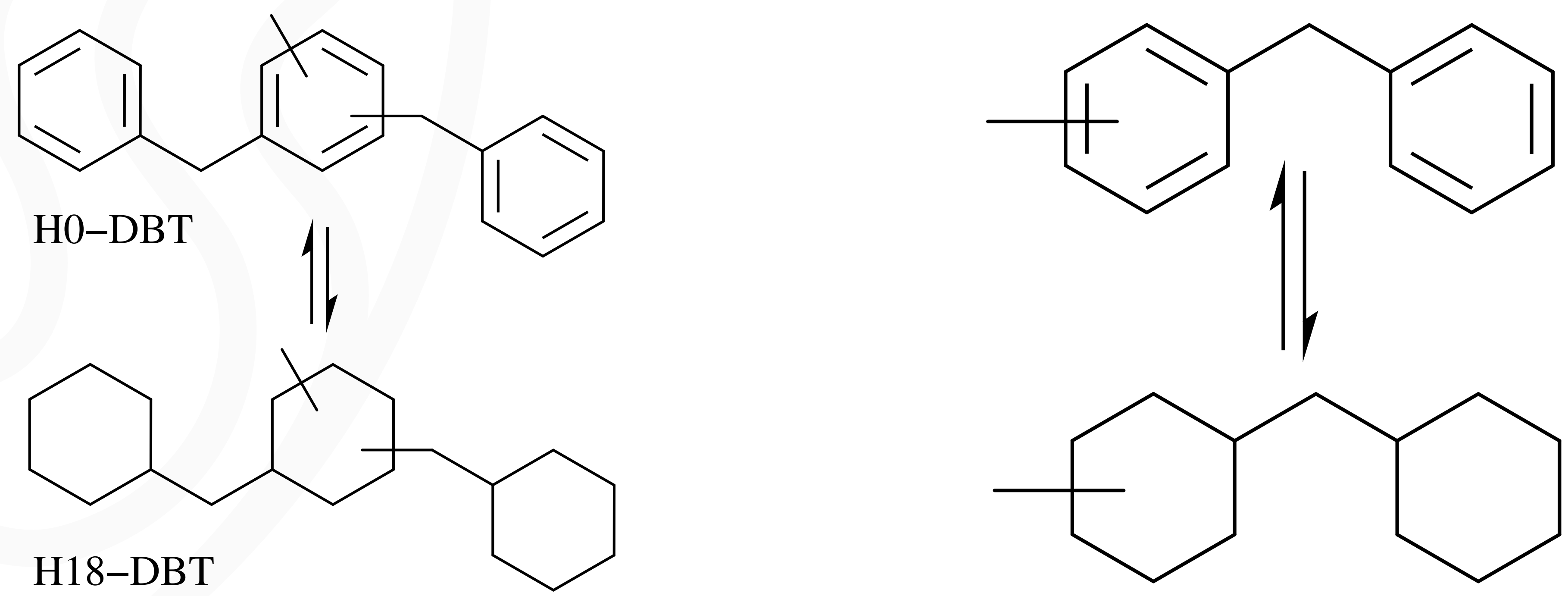
Few developments dedicated to Benzyltoluene/H12-BT.

System much less studied than H0-DBT/H18-DBT, should be less complex.



- High volumetric storage density (54.5 kgH_2/m^3 at RT)
- Liquid in a large range of T°C (-70 to +270°C)
- Excellent robustness in hydrogenation/dehydrogenation cycles
- Low viscosity for easy handling
- Reaction rates (Hyd/Dehyd) higher compared to those of the DBT-based LOHC system (same conditions).

Ircelyon *T. Rüde et al. Sustainable Energy Fuels, 2022, 6, 1541-1553*

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Some ideas in the literature:

- WOx-incorporated $Pt/Al_2O_3 > Pt/Al_2O_3$ (H18-DBT)
  C. H. Kim et al. Fuel, 2022, 313, 122654
- Ni-modified catalysts active (MCH)
  Y. K. Gulyaeva et al. Cataysts, 2020, 10, 1198

Strategy followed for the UnLOHCked project:

- Develop bimetallic catalysts (NiZn, NiCu, NiSn but also PtSn, PtNi)
- Develop single-atoms catalysts
- Develop hydrogen spillover (Hsp) zeolites
- Re, Fe, Mo, Zr mono and bimetallic catalysts (with Pt). Conventional preparation (IWI) and $ScCO_2$ preparation

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Bimetallic catalysts

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NiCu and NiZn known to selectively dehydrogenate methyl-cyclohexane.
2nd metal allows an increase of selectivity compared to Ni alone.

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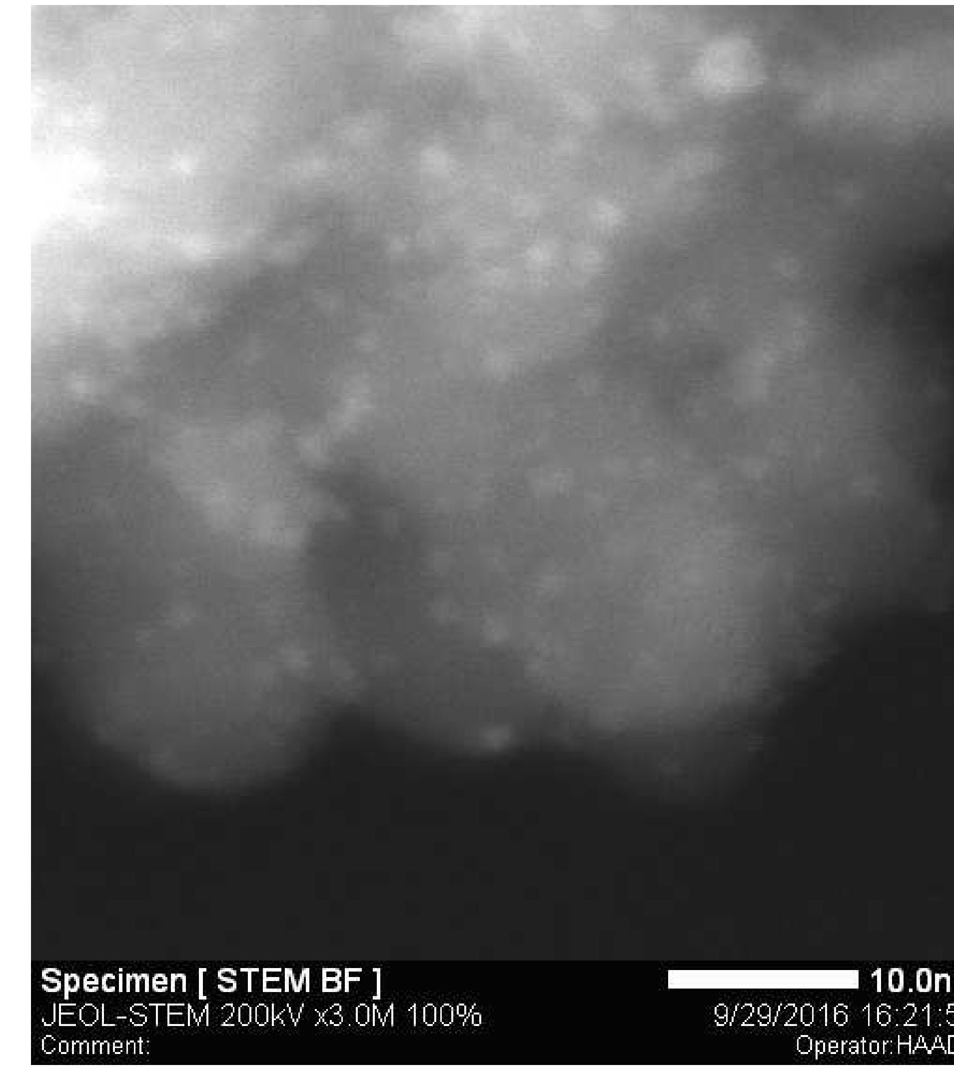
Stategy:
- co-impregnation
- 2-steps SOMC chemistry
- Preparation of Ni silicide NPs in solution further immobilised onto supports

=> different sizes (from 1.5 to 20-50 nm) and different alloy phases.



STEM-HAADF of Ni/SiO_2

NiZn: Al-ShaikhAli, A. H. et al. Chem. Commun., 2015, 51, 12931-12934
NiCu: Gulyaeva, Y. K. et al. Catalysts, 2020, 10, 1198
SOMC: Docherty, S. R. et al. JACS Au, 2021, 1, 450-458
Ni NPs: Galeandro-Diamant, T. et al. Catal. Sci. Technol., 2019, 9, 1555 - 1558

CP2M Catalyse, Polymérisation Procédés & Matériaux

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Single-atom catalysts...

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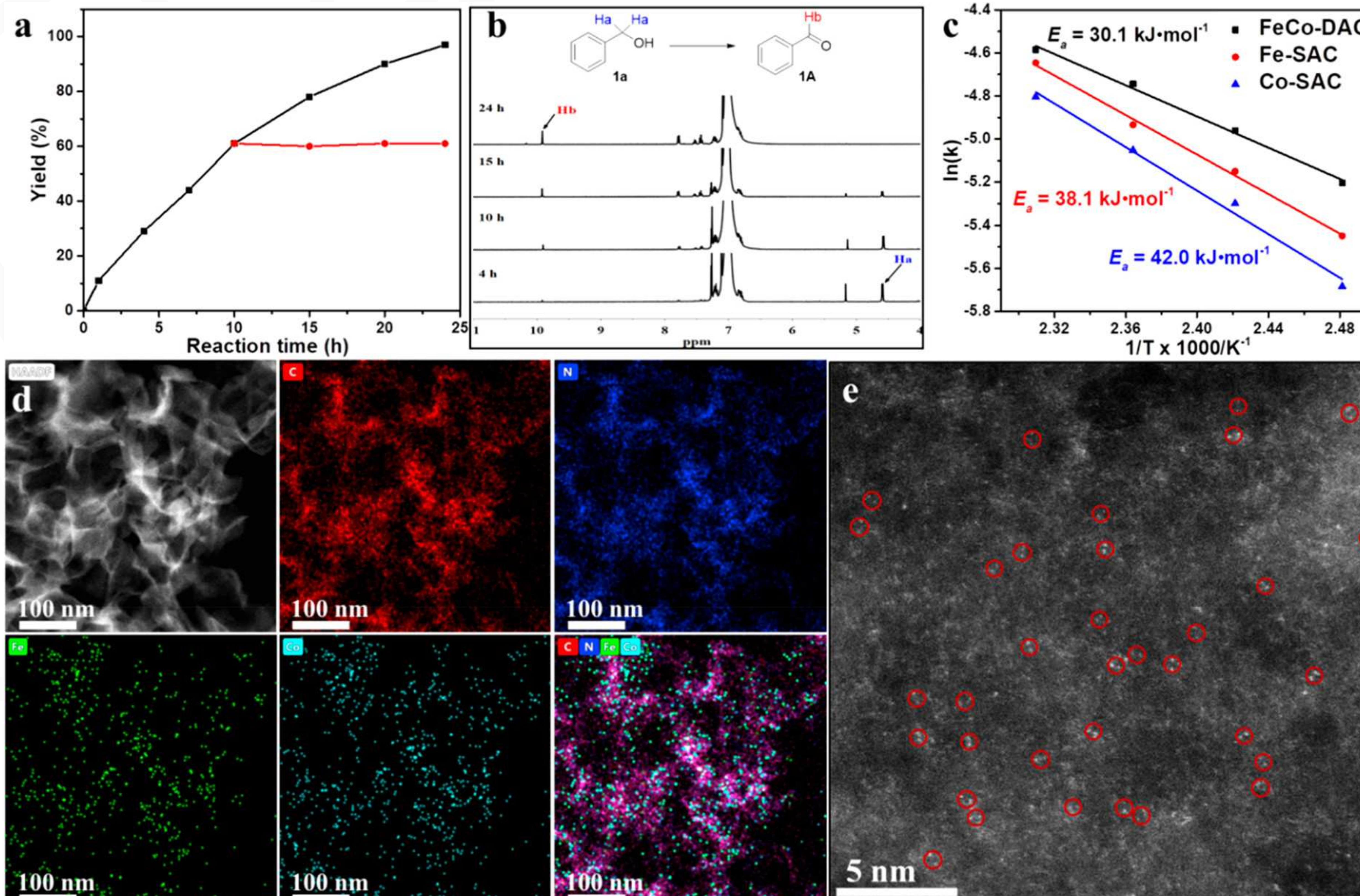
Size below the cluster and nanoparticles => single-atom catalysts



Liu, C. et al, JACS, 2022, 144, 4913-4924

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...or nano-clusters

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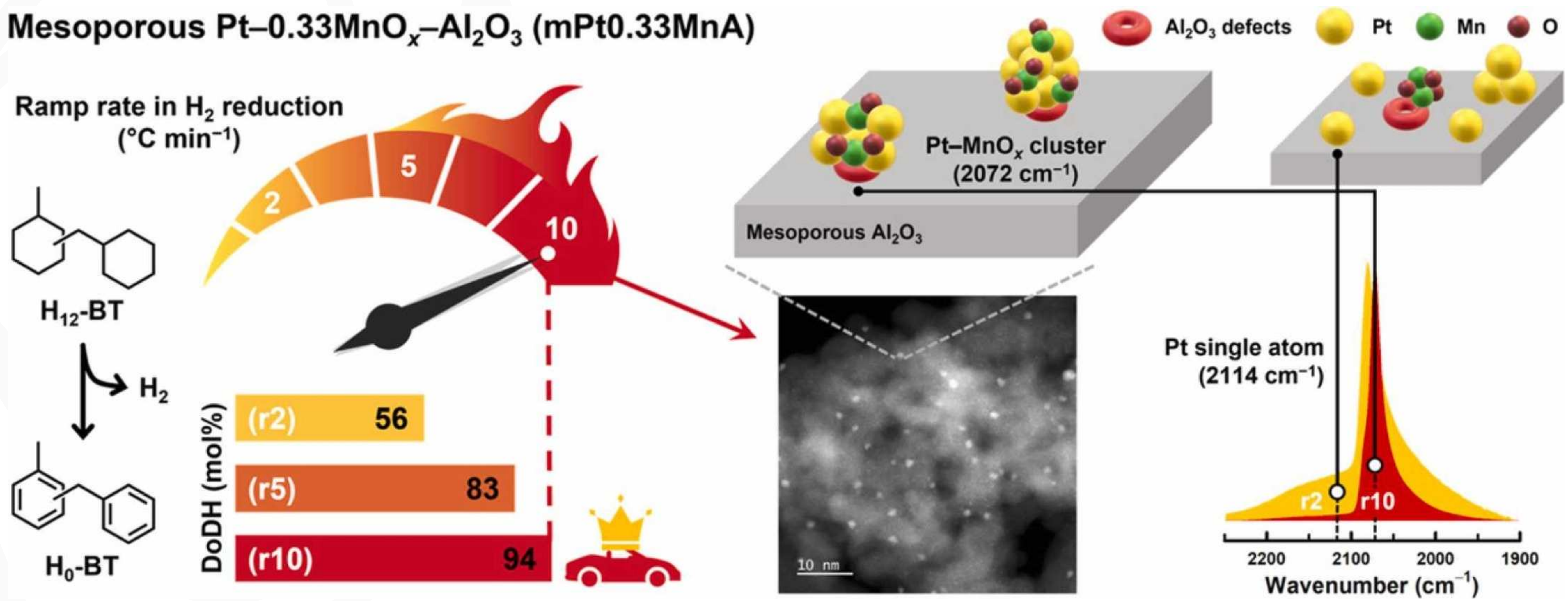

- The higher ramp rate in H_2 reduction of mPtMnA leads to activity improvement.
- Pt nanoclustering with MnOx (< 2 nm) favored

Jo, Y. et al, Appl. Catal. B, 2023, 334, 122848

Hsp supports for hydrogenation

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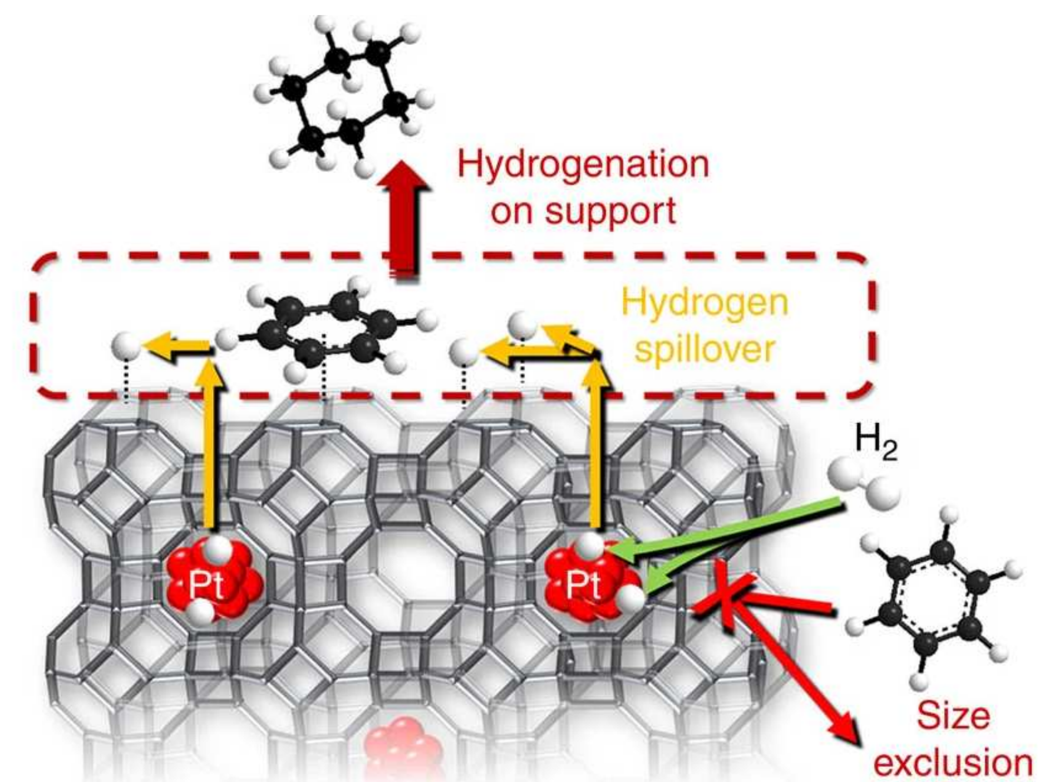
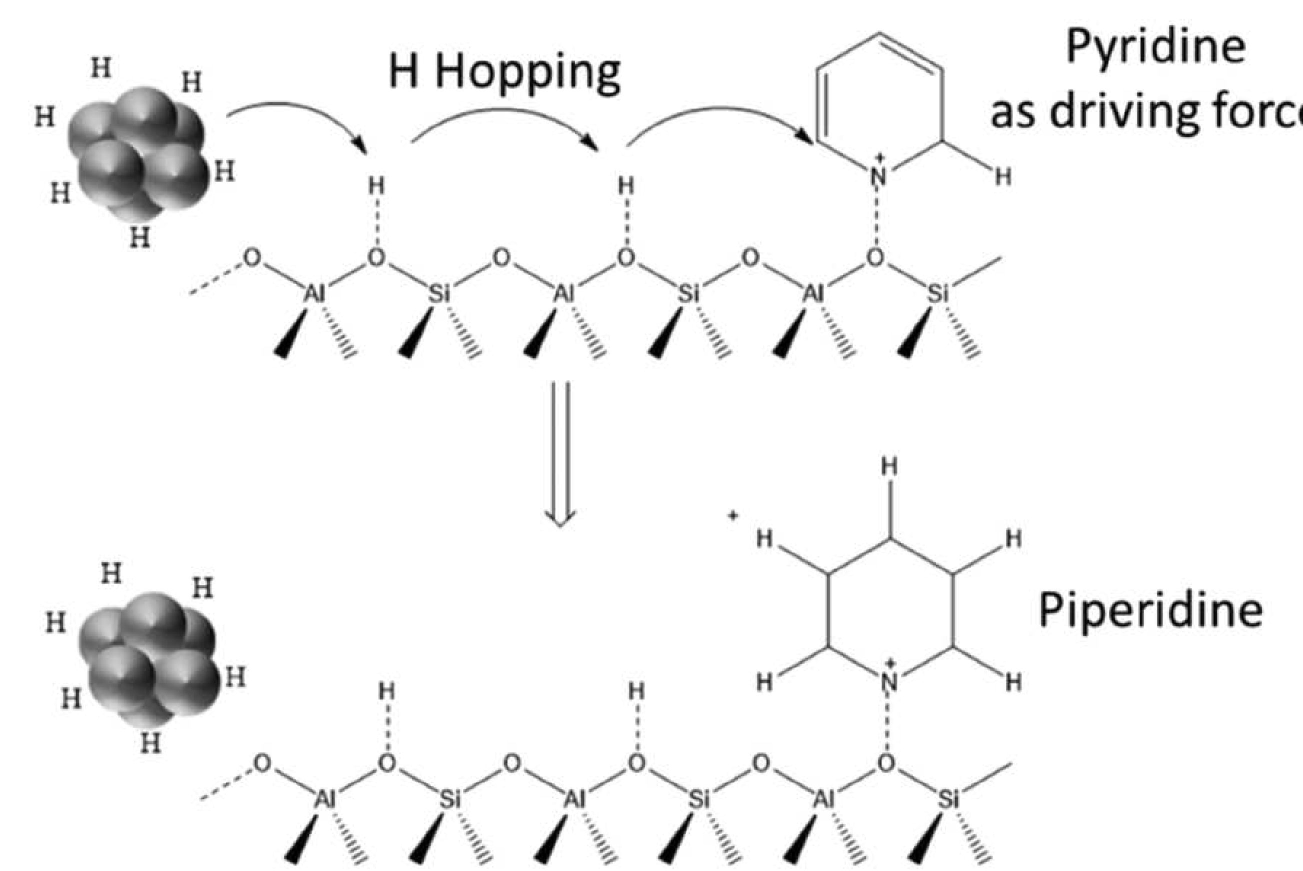
MFI and CHA, supporting metal nanoclusters (size < 2 nm)
Hydrogen spillover phenomenon to enhance the active phase.

Compromise between H_2 diffusion and H spillover
=> modification of the standard zeolite properties:

- Brønsted acidity
- Si/Al ratio
- Extra framework aluminum
- Si-OH

Batalha, N. et al. Catal. Sci. Technol. 2022, 12, 1117-1129
Im, J. et al. Nature Communications, 2014, 5, 3370





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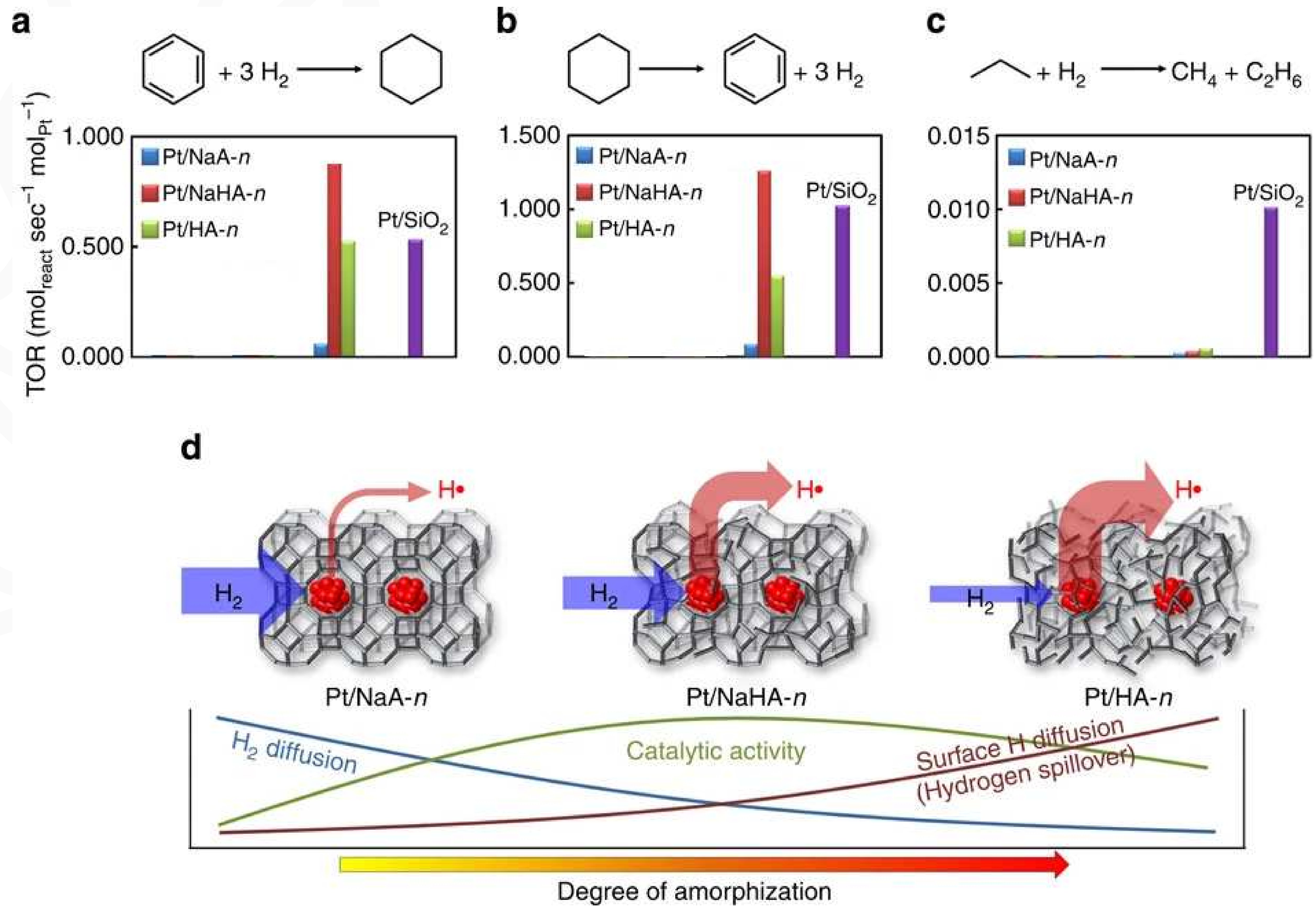
Dehydrogenation enhanced by reverse hydrogen spillover



Im, J. et al. Nature Communications, 2014, 5, 3370

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- UnLOHCked kick-off meeting on July
- Catalyst development from July 2023 to July 2025
- Upscaling of the best catalyst(s) by Heraeus
- Coupling with SOFC
- Demo end 2026

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Thanks to:

- Antoinette Boréave
- Marlène Fabre
- Guillaume Fabre
- Franck Morfin
- Laurent Veyre

European Commission

THANKS FOR YOUR ATTENTION

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Short-symposium "Catalytic reactions for hydrogen storage and release" (R. Janot, N. Bion, V. Meille...).

- LOHC
- Circular storage (NH_3)
- Solid-state H_2 storage: Catalytic reactions to enhance the dehydrogenation

PARTICIPATE TO ICC 2024 in LYON!

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